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(71) Applicant

Imperial Chemical Industries PLC

(Incorporated in United Kingdom)

Imperial Chemical House, Millbank, London SW1P 3JF

(72) Inventors

Bruce Murray McIntosh

Frederic Neil Cogswell

(74) Agent and/or Address for Service

Raymond Hulse,

Imperial Chemical Industries PLC, Legal Dept: Patents,

PO Box 6, Bessemer Road, Welwyn Garden City,

Hertfordshire AL7 1HD

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(54) **Filamentary yarn and film of an aromatic polyetherketone**

(57) A process of melt spinning a yarn or of extruding a film from an aromatic polyetherketone in which prior to spinning or extruding, there is admixed with the polyetherketone polymer in excess of 2% by weight of a plasticiser which is thermally stable at the temperature of the melt and provides a melt of reduced viscosity such plasticiser having volatility characteristics such that though some of the plasticiser volatilises from the spun yarn or extruded film during the process, more than 1% by weight of the plasticiser remains in the spun yarn or extruded film.

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SPECIFICATION

Filamentary yarn and film of an aromatic polyetherketone

- 5 This invention relates to the melt spinning of mono- and multi-filament yarns and to the extrusion of a film from an aromatic polyetherketone and more particularly an aromatic polyetheretherketone. 5

We have found it possible to produce extruded products, more particularly melt spun textile filaments, of an aromatic polyetherketone and more particularly an aromatic polyetheretherketone by conventional melt spinning techniques. This involves melting either a powder or granules of the polymer at between 350°C and 400°C and, using a metering screw or pump, passing the melt to a filter pack where the melt is filtered through graded sand, graded gauzes or sintered metal having a pore size down to about 25 microns. The molten polymer is then extruded through a spinneret at 370°C to 400°C into filaments which are drawn down in a controlled cooling environment. Subsequent processing may involve a reheating of the filaments above 150°C and the drawing of the filaments by a factor of about 3 to complete orientation of the filaments. Film can be produced in a similar manner using a slot die rather than a spinneret. 10 15

However with such techniques we have found it becomes increasingly difficult to produce filaments below 100 microns and more particularly below 50 microns. In the production of filaments 'raining' from the spinneret occurs causing very short lengths of increased diameter to occur in the spun filaments at draw down and it is suspected that the breaks which occur both in the extrusion draw down and in the orientation zone are associated with these discontinuities. This, we have found, limits the fineness of the filaments of polyetheretherketone that can be produced to between 50 and 100 microns depending on the effectiveness of the filtration used. 20 25

In the production of thin films using a slot die instability of the melt curtain edge occurs at thicknesses of about 20 microns and below.

In European Patent Application No 83304022.3 there is described a process of producing a fibre-reinforced composition comprising passing a plurality of continuous filaments of, for example, glass or carbon, through a melt comprising a mixture of a thermoplastic polymer, such as an aromatic polyetheretherketone, and a plasticiser which is thermally stable at least up to the temperature of the melt and having volatility characteristics such that the plasticiser can be volatilised from the composition below the decomposition temperature of the thermoplastic polymer but has sufficiently low volatility at the temperature of the melt to plasticise the polymer and provide a melt of reduced viscosity compared with the melt viscosity of the polymer alone. 30 35

We have now found that the addition of substantial quantities of a plasticiser as used in the process described in European Patent Application No 83304022.3 to a polyetherketone and more particularly a polyetheretherketone before it is melt spun gives rise to a very much more regular extrusion for otherwise similar processing conditions. In addition work done by the extruder screw is reduced considerably and it is possible to reduce the extruder temperature. Consequently we have found using the modified process that filament diameters in the range 20 to 50 microns can be produced without frequent filament breaks. 40 45

According to the invention, therefore, we provide a process of melt spinning a mono- or multi-filament yarn or of extruding a film from an aromatic polyetherketone and more particularly an aromatic polyetheretherketone in which, prior to spinning or extruding, there is admixed with the polyetherketone polymer a substantial proportion of a plasticiser which is thermally stable at the temperature of the melt and provides a melt of reduced viscosity compared with the melt viscosity of the polymer alone such plasticiser having volatility characteristics such that though some of the plasticiser volatilises from the spun yarn or extruded film during the process, more than 1% by weight of the plasticiser remains in the spun yarn or extruded film. 45 50

It will be realised, therefore, that in the process all of the plasticiser is not removed the yarn or film and indeed, for certain applications, there are advantages to be gained from this. 50

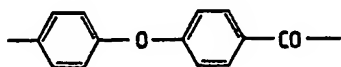
We also provide a melt spun mono- or multi-filament yarn or an extruded film of an aromatic polyetherketone and more particularly an aromatic polyetheretherketone containing in excess of 1% by weight of a plasticiser having the above defined stability and volatility characteristics. 55

Such a yarn or film can be readily converted into a porous yarn or film by an elevated heat treatment process between 250°C and 300°C preferably under vacuum. 55

According to another aspect of the invention, therefore, we provide a porous yarn or film of an aromatic polyetherketone and more particularly an aromatic polyetheretherketone.

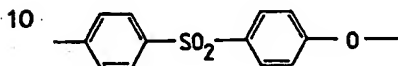
By the term "substantial" which is used in connection with the proportion of plasticiser which is admixed with the polyetheretherketone polymer we mean that in the melt prior to spinning or extruding there is present in excess of 2% by weight of the plasticiser. 60

Suitable polyetherketones for use in the invention include those which contain the recurring unit (I):



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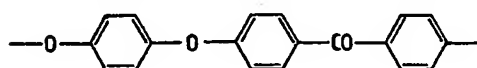
Such polymers are disclosed, inter alia, in British patent specification 1 414 421 which describes such polymers containing the unit (I) as the sole repeating unit or in conjunction with the repeating unit (II):



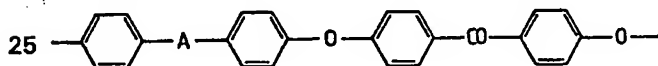
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A preferred polyetheretherketone having the repeating unit (III):

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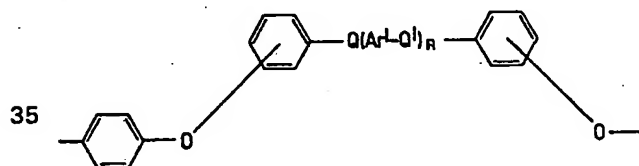
either alone or in conjunction with other repeating units is disclosed in European patent publication No 1879. The other repeating units present in the polymers described in the European application may be of the repeating unit (IV):



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where A is a direct link, oxygen, sulphur, $-\text{SO}_2-$, $-\text{CO}-$ or a divalent hydrocarbon radical. The repeat units may also be of formula (V):

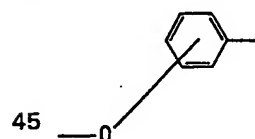
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where the oxygen atom in the sub-units:

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are *ortho* or *para* to the groups Q and Q', Q and Q' which may be the same or different are $-\text{CO}-$ or $-\text{SO}_2-$, Ar' is a divalent aromatic radical, and n is 0, 1, 2 or 3.

The plasticisers which are suitable for use in the invention are materials which are thermally stable at the melt temperatures of polyetheretherketone and which can be partially volatilised from yarns or films during the production thereof in accordance with the invention process. Apart from that the plasticisers used will essentially have the capability of providing a plasticised polymer melt of lower melt viscosity than the polymer itself. Suitable plasticisers having these characteristics are found in the classes aromatic ketones, aromatic sulphones and aromatic esters. Typical plasticisers in these classes are diphenyl sulphone, ditolyl sulphone, benzophenone, phenyl benzoate and benzyl benzoate.

The plasticiser and polymer may be admixed by any conventional technique. For example, a mixture may be achieved:— by dry blending the polymer and the plasticiser, by compounding in a screw extruder, by coating granules of the polymer with a solution of the plasticiser and volatilising the solvent from the coated granules or in suitable cases by adding the plasticiser in the course of producing the polymer.

As mentioned above the mixture of the plasticiser and the polymer will have a reduced melt viscosity compared with the melt viscosity of the polymer alone. Furthermore we have found that the addition of the defined plasticiser serves to greatly reduce the tendency of the melt to

gel and this contributes to improved processing particularly with a low decitex per filament yarn.

It will of course, be realised that the properties of yarns produced according to the invention will be influenced by the fairly high residual level of plasticiser present. Though the presence of the plasticiser in the filaments of the yarn will detract from their fibre strength, we believe that where the filaments are to be used in a composite yarn structure with, for example, carbon fibre this could offer advantages by reducing the density of the polymer forming the filaments and also by promoting the wetting out of the carbon fibres. We also believe that multifilament yarns produced by the process of the invention would find application in fabrics for special industrial end uses.

10 Polyetherketone films produced by the process of the invention include any film produced by a melt extrusion process and may be in substantially amorphous form or may be in molecularly oriented form, such as that resulting from drawing a substantially amorphous film of the polyetherketone. A substantially amorphous film may be achieved by quenching a film produced by melt extrusion on to a cold casting drum. The film may be drawn uniaxially or biaxially. Normally the sheet, if drawn, will be drawn in two directions, the first direction being the direction of extrusion (sometimes termed the 'machine direction' (MD)), the second direction being transverse to the machine direction (sometimes termed 'transverse direction' (TD)). Details of preferred processes for forming oriented films of polyetherketones are disclosed in Research Disclosure 21601, April 1982.

20 Typical conditions for the production of a substantially amorphous film by the process of the invention include the extrusion of a molten mixture of the polyetherketone and a melt plasticiser as specified through a slot die with take up of the film on a cooling drum maintained at a nominal temperature of 35°C. The quenched substantially amorphous film may then be subjected to uniaxial or biaxial stretching procedures whilst the film is maintained at a temperature above the second order transition temperature (T_g) of the polyetherketone. In the case of a polyetherketone of repeat unit $-O-Ph-O-Ph-CO-Ph-$ (Ph is p-phenylene) (available from Imperial Chemical Industries as 'Victrex' PEEK) the drawing, if performed, should be conducted at a temperature of between 140° to 200°C. If a temperature in excess of 200°C is used the film tends to crystallise prematurely giving rise to unacceptable films.

30 The drawn films of the invention may be heat set, that is caused to crystallise whilst being restrained from shrinking. For 'Victrex' PEEK appropriate temperatures for the heat step process are in the range 200°C to 320°C.

The main advantage of the present process over that disclosed in Research Disclosure 21601, April 1982 is the co-melt of polyetherketone and plasticiser has viscosity characteristics which are significantly different from those of the melt of the polymer alone and this enables film of much improved quality to be obtained. Additionally the co-melt may be fabricated at lower temperatures than that of the melt alone with consequential benefits. The advantageous viscosity characteristics of the co-melt and the fact that much of the plasticiser can be removed from the film after extrusion offer the benefit of being able to obtain thinner films by the process of the invention.

The films of the invention will inevitably contain plasticiser as they emerge from the extrusion die and provision for removing the plasticiser to an extent consistent with the final application of the film is required. The most convenient means for removing plasticiser makes use of the volatility of the plasticiser employed at temperatures below the decomposition of the polymer. Volatilisation or partial volatilisation of plasticiser may be effected after the co-melt emerges from the die and before it is quenched, by maintaining its temperature above the volatilisation temperature of the plasticiser for a sufficient time to allow for volatilisation of the plasticiser.

Alternatively, removal may be effected by heat treatments which occur as a part of the drawing and heat setting procedure or in additional heat treatment steps. For some applications if may be necessary to provide additional treatments such as solvent extraction, particularly where it is required that the plasticiser content should be less than 1% by weight of the film.

EXAMPLE

Process A was carried out on conventional spin-draw equipment with the object of producing 65 f9 multifilament yarn from polyetheretherketone polymer ('Victrex' (Registered Trade Mark) polyetheretherketone polymer, 150P grade, obtainable from Imperial Chemical Industries PLC.

The process used was a conventional one for spinning a low dpf yarn from a thermoplastic polymer (see conditions below). There was considerable 'raining' evident from the spinneret—at least one slub per filament per metre was perceived just below the spinneret. Furthermore the process was unstable with frequent threadline breaks occurring (at least one per minute) in the extrusion and draw zones.

Process B was carried out in a similar manner to Process A except that 30 parts of powdered diphenyl Sulphone was mixed with 70 parts of the same polyetheretherketone polymer prior to drying and feeding to the machine hopper (in the manner of Process A).

65 The main advantages achieved with Process B compared with Process A was the elimination

of 'raining' from the spinneret and a dramatic improvement in the threadline interruption rate so that a practical process performance was achieved. In addition the power requirements of the screw dropped and it was also possible to drop the extrusion temperature to 340°C which is well below that possible for any conventional processing of polyetheretherketone.

5 The processing conditions for Process A and Process B are listed below. 5

	<i>Process A</i>	<i>Process B</i>	
	Screw Speed	2.0 rpm	
	Screw Current	1.5 amps	
10	Melt Temperature	320–380°C	10
	Extrusion Temperature	380°C	
	Pack Filtration	2 × 200 mesh screens	
	Spinneret	9 hole 0.64 mm dia	
	Feed Roll Speed	32 mpm	
15	Feed Roll Temperature	150°C	15
	Draw Roll Speed	90 mpm	
	Decitex	65 f9	
	% Diphenyl Sulphone in Fibre	0.01%	

20 CLAIMS

1. A process of melt spinning a mono- or multi-filament yarn or of extruding a film from an aromatic polyetherketone in which, prior to spinning or extruding, there is admixed with the polyetherketone polymer a substantial proportion of a plasticiser which is thermally stable at the temperature of the melt and provides a melt of reduced viscosity compared with the melt
- 25 viscosity of the polymer alone such plasticiser having volatility characteristics such that though some of the plasticiser volatilises from the spun yarn or extruded film during the process, more than 1% by weight of the plasticiser remains in the spun yarn or extruded film. 25
2. A process as claimed in Claim 1 in which the aromatic polyetherketone is an aromatic polyetheretherketone.
- 30 3. A process as claimed in either Claim 1 or Claim 2 in which the plasticiser is diphenyl sulphone. 30
4. A melt spun mono- or multi-filament yarn or an extruded film of an aromatic polyetherketone produced by the process of Claim 1 or Claim 3.
5. A melt spun mono- or multi-filament yarn or an extruded film of an aromatic polyetheretherketone produced by the process of Claim 2 or Claim 3. 35
6. A porous yarn or film produced by subjecting the yarn or film as claimed in either Claim 4 or Claim 5 to a heat treatment process.